Synthesizing zeolites from power plant waste

Doing Alchemy with Ash

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Power-plant waste products can in fact prove useful in purifying the environment, and even in washing our dirty laundry. Zeolites, an important component used in washing powders, can be obtained from the "fly ash" generated by power plants

Zeolites, a type of tectosilicate, are minerals with unusual properties: the insides of their crystals contain a network of channels several atoms wide which can host individual gas molecules, hydrated metal ions, or small organic compounds. The channels running through a single gram of zeolite crystal lattice can sometimes have a total surface area of even 1,000 m^2. These channels are also negatively charged, and can form weak bonds with various cations, which can be exchanged in a wide range. Because zeolite structures can adsorb vast quantities of ions, they are put to use in a great many branches of industry as adsorbents or molecular sieves.

Zeolites can be obtained in one of two ways: they can be mined from natural deposits, or synthesized in the laboratory. While the largest zeolite deposits are of hydrothermal origin (with hot volcanic aqueous solutions being involved in their crystallization), zeolites do also crystallize in certain lakes, bays cut off from the sea, and alkali soils in warm, intermittently dry climates. The substrate involved in zeolite crystallization consists of silicates that are unstable in such environments, such as volcanic lava minerals or clay minerals.

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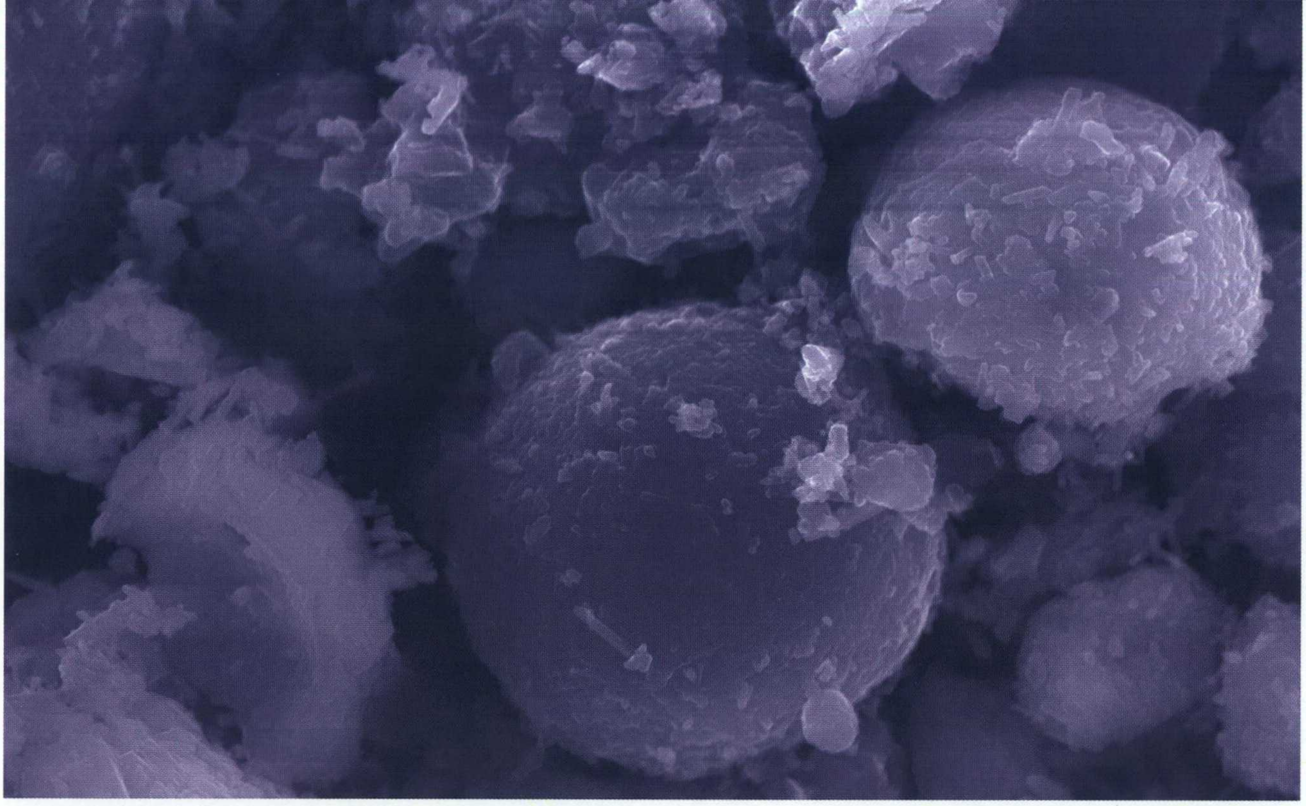
Coal, when combusted, leaves a lot of very thin ash called "fly ash." This residue, being dumped as waste by power plants, can be used to produce cheap synthetic zeolites

Artificial is better

The most common naturally occurring mineral in the zeolite group is clinoptylolite. While Poland possesses its own clinoptylolite sources, for economic reasons this mineral is in fact imported from southern Slovakia, Hungary, or Ukraine. Natural zeolites unfortunately have limited application, because their properties are strictly dependent upon their crystal structure, which is quite invariable in natural deposits. Their chief shortcoming is that their micropore diameter is too small (circa 0.3-0.4 nm), thus hampering their ability to adsorb larger gas molecules or organic compounds. On the other hand, clinoptylolite is indeed very effective in adsorbing heavy metals and ammonium ions, and thus finds applications both in the purification of mine water and in eliminating unpleasant odors from household pet waste.

Nevertheless, modern industrial technologies require molecular sieves and adsorbents with very precisely specified parameters, necessitating the artificial production of synthetic zeolites and other "zeolite-like" materials. Such synthesis reactions take the proper equipment, pure substrates, plus energy - and the cost involved might therefore be as much as several thousand times higher than the price of natural zeolites. This is why research concentrates on seeking cheap and available substrates (such as kaolinite) for use in zeolite production, while at the same time striving to reduce the costs of the operation itself.

One very promising material for producing zeolites is called "fly ash" - the lightest fraction of the waste obtained by coal combustion, which is trapped by the electrostatic filters in plant chimneys. A large electric power plant, working at peak, can produce as much as 1,000 tons of fly ash per day. Fly ash chiefly consists of aluminosilicate glass, quartz, and mullite, formed from the mineral impurities present in the coal fuel. It may also contain a variable quantity of gypsum, depending on the combustion technology employed. Aside from this latter component, which is eagerly used by factories producing bonding



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Glass microspheres covered in crystallizing zeolites

agents, fly ash utilization generally poses a serious problem for most energy producers. Fees are imposed for each ton of this waste so produced. Every ton must furthermore be stored or managed, entailing additional costs that must ultimately be paid by the energy consumer. This means that attempts at harnessing this material for the synthesis of zeolites make excellent sense - especially since its composition is very similar to the rocks that act as the substrate in the crystallization of natural zeolites.

A thousand years in a day

The chief obstacle, however, is not how to transform ash into zeolite per se, but rather the time which such an operation requires. Geological processes last millions of years, and any process that takes less than 100,000 years is described as "instantaneous." Even if we assume the minimal time-frame (i.e. it takes "merely" a few thousand years for natural zeolites to form in intermittently semi-desert lakes), this is still too long to entertain any sort of industrial application. Laboratory synthesis of zeolites from pure substrates takes from a few hours up to a few days (requiring temperatures ranging from 80°C to more than 200°C). And so, the ideal solution would be to identify some sort of "happy medium" between these two sets of conditions, making it possible to obtain a product of complex properties, using low-quality substrates, at a low cost and within a reasonable time-frame.

The research pursued in Poland is innovative in two regards. Firstly, unprocessed ash is used in the synthesis - most of the technologies now being put forward in the world require that the ash be initially melted together with hydroxides at a temperature of 500°C, something which automatically hikes up the production costs and calls the profitability of the entire process into doubt. Secondly, our technique can yield a product rich in zeolites with wide micropores (for instance, of type "X" with a micropore diameter of more than 0.7 nm) and large adsorptive capacity. In terms of their properties, they are superior to any natural zeolites available from European deposits.

Such zeolites and others with unique characteristics were obtained via a 24-hour reaction at a temperature of 60-70°C. The low temperature means that high-pressure vessels do not need to be used in the production process. Further research has enabled us to develop a procedure for zeolite crystallization at room temperature. This requires the suspension to be stored for several months, but the advantage here is that large quantities of product can be obtained at a very low cost. This procedure offers a good alternative to low-temperature hydrothermal technology. The resulting product's active phase content has as yet not exceeded 60%, but this quality suffices for many industrial applications.

Another successful example is the synthesis of a sodalite-type zeolite - i.e. one that is characterized by narrow micropores, but also by a large ion-exchange capacity and stability at high temperatures - using a wetting-and-drying procedure. While supplying a small quantity of heat in a form that imitates solar radiation, one can use this method to obtain a pure zeolite product of this sort in three days.

The estimated cost of obtaining zeolite material using the above mechanisms ranges between that of natural zeolites and that of synthetic ones. However, bearing in mind that the fees for processing, storing, and utilizing ash will probably be on the rise, the implementation of one of these technologies could ultimately prove to be the most profitable solution. ■

Further reading:

Derkowski A., Franus W. (2004). Properties of Na-X zeolite materials produced from coal fly ash by low temperature and hydrothermal methods of synthesis. *Polish Journal of Environmental Studies*, 13 (III), pp. 28-30.